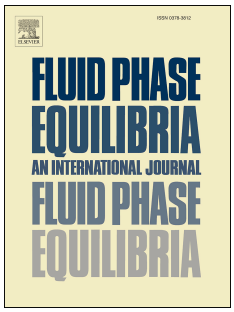

Comments on the Correlation of Vapor-Liquid Equilibrium (VLE) Data in azeotropic ternary systems

A. Marcilla, M.M. Olaya, J.A. Reyes-Labarta

PII: S0378-3812(16)30060-7

DOI: 10.1016/j.fluid.2016.02.010

Reference: FLUID 10999

To appear in: *Fluid Phase Equilibria*

Received Date: 9 November 2015

Revised Date: 22 January 2016

Accepted Date: 8 February 2016

Please cite this article as: A. Marcilla, M.M. Olaya, J.A. Reyes-Labarta, Comments on the Correlation of Vapor-Liquid Equilibrium (VLE) Data in azeotropic ternary systems, *Fluid Phase Equilibria* (2016), doi: 10.1016/j.fluid.2016.02.010.

Comments on the Correlation of Vapor-Liquid Equilibrium (VLE) Data in azeotropic ternary systems

A. Marcilla*, M.M. Olaya and J.A. Reyes-Labarta

Chemical Engineering Department, University of Alicante, Apdo. 99, 03080 Alicante, Spain.

*Corresponding author: Tel.: (34) 965 903789. E-mail: Antonio.Marcilla@ua.es.

Abstract

The analysis has been carried out of the possible theoretical types of ternary systems regarding the distillation boundaries, for systems involving up to three binary azeotropes and one ternary azeotrope. The study reveals that there are some of these theoretical behaviors that classical activity coefficient models such as NRTL cannot predict. The objective of the present work is to show these limitations, analyze their causes and suggest possible solutions. The addition of one ternary interaction term to the Gibbs energy of excess function removes many of the limitations of classical models expanding the number and type of systems that could be correlated with the models and, what is more important, markedly improving the correlation capability of the model.

Keywords: phase equilibria, VLE, LLE, data correlation, activity coefficient, NRTL model.

Introduction

Correlation of phase equilibrium data is a very important issue with relevant applications in chemical engineering, such as the design of separation equipment. Accurate description of vapor-liquid equilibrium (VLE) plays a major role in industrial separation processes. Efficient design and operation of distillation and rectification processes are based upon these equilibrium data. Due to this important practical application, an extensive number of papers have been dedicated to the experimental determination and correlation of VLE data for many binary and multicomponent systems and to a lesser extent of VLLE data. The multivolume DECHEMA series [1] is a very popular compilation of experimental phase-equilibrium data. The Dortmund Data

Bank (DDB) contains nearly all worldwide available phase equilibrium data [2]. The NIST SOURCE Data Archival System [3] implements all major principles of the concept of dynamic data evaluation which combines a large electronic database of equilibrium data with expert software designed to generate recommended data.

The correlation of the experimental equilibrium data using an empirical or physically grounded equation allows the interpolation and, with caution, extrapolation of equilibrium data to new conditions of temperature and pressure. The thermodynamic equations used to correlate and predict VLE data are classified as excess Gibbs energy (G^E) models, also named activity coefficient models, and equations of state (EOS). Classical models to represent the activity coefficient for the liquid phase, or equivalently the excess Gibbs free energy (G^E) that are used for VLE calculations are: Margules [4], van Laar [5], NRTL [6] and UNIQUAC [7]. Another classical model such as the Wilson equation [8] can be used in the VLE calculations but not for LLE and VLLE due to the incapacity of this equation to produce liquid-liquid splitting. All these are activity coefficient models used nowadays and they are exactly the same as those used thirty or forty years ago, although the development of EOS has been much more relevant in the last years. This fact could suggest that the results obtained with the classical models to formulate the non-ideality of the liquid phase are sufficiently accurate and no relevant limitations are found. Nevertheless, this is not the case despite the significant contribution of these models to phase equilibrium data modelling during the past four decades, particularly NRTL and UNIQUAC. Many important limitations exist that have already been widely discussed in the literature [9,10]. Following, we summarize the most important ones:

1. The activity coefficient models based on binary parameters have been developed with the aim of extrapolating from binary to multicomponent mixtures, but the facts show that very poor or uncertain results are obtained in these phase equilibria predictions. Therefore, the potential main value of these models is not achieved in practice. As a consequence, group contribution methods such as UNIFAC are used for phase equilibrium predictions involving liquid phases and local composition models such as NRTL and UNIQUAC are restricted to the experimental data correlation.

2. For many systems these models cannot achieve a precise representation of the equilibrium data, as it is required, for example, for separation processes design. Many

examples of this can be found for VLE and LLE correlations of types 1 and 2 (Treybal classification [11]), to mention exclusively the most simple fluid phase equilibria [12] . When the complexity of the system increases, the restrictions are even higher. For example, as far as we know, commercial equilibrium data regression tools do not allow for the simultaneous regression of different equilibrium regions in type 3 and 4 ternary systems (Treybal classification [11]), neither data regression of island type ternary systems. For example, ChemCAD [13] specifies that it only deals with the regression of type 1 and 2 systems. It seems that the reason is a deficient quantitative description of these types of systems by means of these models, as we discussed in [14, 15].

3. The simultaneous description of VLE and LLE data is too frequently not possible [16] [9]. In this respect Sandler says in his book [17]: “There can be some qualitative and quantitative inconsistencies when correlating LLE data and then using the parameters obtained to predict VLLE. This is why in the predictive UNIFAC model, there is one set of parameters only for use in vapor–liquid equilibrium predictions and a separate UNIFAC-LLE parameter set only for LLE predictions”. This limitation is relevant because the design of separation processes requires a unique set of parameters able to represent all the different equilibrium regions.

Many modifications of the classical models have been published which use different approaches to develop the mathematical functions for the dependence of the activity coefficients with composition and temperature, as for example: Rarey [9], Gebreyohannes et al. [18] and Neau et al. [19]. However, these and other similar modifications to the classical activity coefficient models do not seem to have influenced thoroughly the later work in this area of the phase equilibrium calculations. For instance, the activity coefficient models included in ThermoData Engine (TDE) [20], quite recent software to generate recommended data and model parameters based on experimental data from NIST SOURCE, are the classical ones.

In some recent papers we have tried to go further into the reasons for all these limitations of the classical Gibbs energy of mixing models, in an attempt to modify them or propose new ones really capable of overcoming these restrictions. We have selected NRTL as a representative model of the classical activity coefficient equations because among equations for the excess Gibbs energy, it is considered as that which

offers the best balance between simplicity, reliability and applicability to numerous mixtures [21]. Some of the most important conclusions are the following:

1. NRTL present "gaps" in the G^E function for miscible binary mixtures, and consequently in the Gibbs energy of mixing (G^M) sum of the ideal (G^{id}) and excess (G^E) contributions. These gaps are the true reason for the impossibility of fitting many VLE and LLE data for many binary, ternary and multicomponent systems, as we have shown in papers [10, 22].

2. Many topological conditions must be fulfilled by the G^M function, as is required by the tangent line (plane or hyper-plane) criterion for two (three or more components), respectively, in order to simultaneously reproduce different type of equilibrium regions. For example, VLE and VLLE of ternary systems with the presence of binary and ternary azeotropes; LLE and LLLE in type 3 (Treybal classification [11]) systems, LLE in island type ternary systems where liquid splitting in the ternary mixtures must be compatible with homogeneity in the three binary ones. Many more examples could be mentioned if this analysis is extended to the presence of solid phases with the possibility of different hydrates as in the case of type 4 (Treybal classification [11]) systems. These difficulties frequently lead to poor results when all the equilibrium regions are simultaneously regressed using a unique set of parameters and, as a consequence, partial fittings are carried out and published for these complex systems.

All this analysis suggests that more flexible models, considering a higher number of molecules interacting and consequently with a higher number of parameters, must be developed, but what is more important: this process should be carried out taking into account the topology required by the G^M function to be able to correctly represent the phase equilibrium behavior of the systems in all the regions to be correlated in accordance with the Gibbs minor common tangent equilibrium criteria. Nevertheless, this higher complexity, and the correspondingly higher number of parameters involved, should not be a limitation nowadays with the also highly improved calculation power of new computers. Consequently, we should remove classical prejudices for G^E models such as: simplicity, two parameters (or very few more) per binary pair and only binary parameters. If primarily the model must represent the experimental data with the required accuracy, these demands could be too severe for the model to adequately represent many equilibrium behaviors that exist in nature. To reinforce these ideas, we

will comment on this peculiar comparison: the pressure vapor of a pure component as a function of temperature, which is a fairly simple continuously growing function for the moderate temperature involved in non-critical VL calculations, is usually represented by at least three parameters (e.g. Antoine's equation) or even more (four parameters in the Wagner vapor pressure equation and five parameters in ChemCAD [13] and other process simulators). Contrarily, the models to represent the complex behavior of the liquid phase activity coefficients required to calculate highly non-ideal or azeotropic systems are restricted to two (or three at most) parameters for each pair of compounds. Therefore, it seems reasonable and convenient to relax some of the requirements traditionally imposed to the activity coefficient models to favor the quality of the results obtained in phase equilibrium calculations, while taking into account the unquestionable advantages of the molecular thermodynamics insight.

Regarding practical and engineered oriented results, it is important to emphasize that better results are not always accomplished with the apparently superior models, as we showed [23] in a study based on the DECHEMA Chemistry Data Series [24] correlation results. For example, the semi-empirical formalisms included in the UNIQUAC model, though it provides the model with a more realistic picture of the liquid mixtures, are not able to give better results than other simple models as Wilson or NRTL, when they are used in the correlation of VLE data.

With this perspective in a recent paper (in press) [25], we have satisfactorily carried out the simultaneous correlation of the experimental equilibrium data for the VLL and VL regions of a ternary system with a unique set of parameters using an extended NRTL equation including a ternary term and a binary correction based on the NRTL equation.

The limitations of the activity coefficient models have two consequences in phase equilibria calculations: a) qualitative but not quantitative description of specific experimental equilibrium data sets, or b) impossibility even in the qualitative description of certain type of systems. In the present paper we address the second issue analyzing the possible theoretical types of ternary systems regarding the distillation boundaries, for systems involving up to three binary azeotropes and one ternary azeotrope. The study reveals that there are many of these theoretical behaviors that equations such as NRTL cannot predict. The objective of the present work is to show these limitations, analyze their causes and suggest possible solutions.

The impossibility of NRTL to represent certain type of azeotropic ternary behaviors

Perry's Handbook of Chemical Engineering [26] presents 125 possible theoretical types of ternary systems regarding the distillation boundaries, for systems involving up to three binary azeotropes and one ternary azeotrope, although only a dozen or so represent most systems commonly encountered in practice. In page 58 of chapter 13 of the seventh edition of this handbook it is stated that "Residue curves can be constructed from experimental data or can be calculated analytically if equation-of-state or activity-coefficient expressions are available (e.g., Wilson binary-interaction parameters, UNIFAC groups)….". Nevertheless, this statement is not completely true since the classical activity coefficient equations such as NRTL cannot predict some of these types of systems, as it is illustrated below.

The causes of such limitation must be searched for in the combination of the particular mathematical equations for the excess Gibbs energy for the liquid phase (e.g. NRTL) and for the vapor phase (e.g. ideal behavior and the liquid phase as the reference state), represented in Eq. (1) and Eq. (2), respectively, and the equilibrium conditions. The equilibrium conditions can be expressed as the equality of the partial derivatives of the G^M function of both liquid ($G^{M,L}$) and vapor ($G^{M,V}$) phases, at the points of tangency of the common tangent plane to both G^M surfaces, for ternary systems. If the system presents azeotropy, in addition to this condition both points merge in a single point for the same composition (z_i) where the energies of both phases $G^{M,L}$ and $G^{M,V}$ are also equal, Eq. (3) and Eq. (4), and z_i is the azeotropic point.

$$G^{M,L} = \frac{g^{M,L}}{RT} = \frac{g^{Mid,L}}{RT} + \frac{g^{E,L}}{RT} = \sum_{i=1}^{c} x_i ln x_i + \sum_{i=1}^{c} x_i \frac{\sum_{j=1}^{c} x_j \tau_{ji} G_{ji}}{\sum_{k=1}^{c} x_k G_{ki}} \quad (1)$$

$$G^{M,V} = \frac{g^{Mid,V}}{RT} = \sum_{i=1}^{c} y_i ln y_i + \sum_{i=1}^{c} y_i \frac{g_i^{pure,V}}{RT} = \sum_{i=1}^{c} y_i ln y_i + \sum_{i=1}^{c} y_i ln \frac{P}{P_i^0} \quad (2)$$

$$\left(\frac{\partial g^{M,L}/RT}{\partial x_i}\right)_{z_i} = \left(\frac{\partial g^{M,V}/RT}{\partial x_i}\right)_{z_i} \qquad \forall i = 1, \ldots . c \tag{3}$$

$$g^{M,L}/RT|_{z_i} = g^{M,V}/RT|_{z_i} \tag{4}$$

The topological point of view may clarify these concepts for selected examples. This analysis could be performed using the Gibbs energy of mixing (G^M) for the liquid and the vapor, as explained above. However, when considering azeotropy the first term in the right part of both equations Eq. (1) and Eq. (2) is the same ($x_i = y_i = z_i$) , to analyze the tangent points between these two functions these terms can be omitted with the advantage that the resulting function for the vapor, referred as G^V, is a plane at constant temperature:

$$G^V = \sum_{i=1}^{c} y_i ln \frac{P}{P_i^0} \tag{5}$$

To show this situation, the isothermal triangular prismatic plot of $G^p=g^p/RT$ (where p indicates the liquid or vapor phases) in the vertical axis versus composition in the base of the prism for ternary systems could be represented for the vapor and the liquid phases representing G^V and $G^{E,L}$, respectively. In this type of representation, the G plane of the vapor phase moves downwards almost in a parallel way as the temperature increases, while the surface corresponding to the liquid phase (that has been considered as the reference state for all the components of the system) remains almost unaltered when the temperature increases. The situation presented in Fig. 1 corresponds to a system of type #47 of Perry's classification [26] involving a ternary minimum boiling point azeotrope (ternary mbpa) and a binary minimum boiling point azeotrope (binary mbpa). In this figure H, I and L are used for the components in the order of their boiling temperatures: H (heavy), I (intermediate) and L (light). For this type of ternary systems, when increasing the temperature ($T_1<T_2<T_3$), the tangency between the G^V and $G^{E,L}$ functions must firstly be obtained in the ternary azeotrope, at T_2 in Fig. 1c, and at higher temperature the tangency will occur in the binary azeotrope, at T_3 in Fig. 1d.

The position of the vapor plane takes into account that the order for G^V is H > I > L as is deduced from Eq. (5) where the vapor pressure increase as follows H < I < L. Considering the topology of this vapor surface G^V and the tangency points required for the ternary and binary mbpa's as a function of temperature, we can observe that Fig. 1c and 1d will only be possible if three conditions are satisfied by the excess Gibbs energy of the liquid surface for these type #47 ternary systems: $G^{E,L}$ must be *positive* and *concave* for all the compositions space but furthermore, it must present a *maximum* in one ternary composition. Moreover, the existence of such a maximum point is not a guarantee for the existence of the ternary mbpa because it also depends on the position of the plane for the vapor phase being possible that the binary azeotrope is obtained at lower temperature. So, concavity with a ternary maximum point in the $G^{E,L}$ surface will be a necessary but not sufficient condition to model type #47 ternary systems. In Fig. 1, the $G^{E,L}$ surface has been qualitatively drawn to present the conditions required by this type of system. In the present paper, we will show that using the NRTL model is not possible to represent this type of system because the conditions required to present only one binary pair with a minimum boiling point azeotrope (mbpa) lead to a $G^{E,L}$ surface unable to give the tangency in a ternary point at lower temperature as it is required by type #47 systems in the Perry's classification [26].

Demonstration of a simplified case

Initially we will consider, as a first step in this demonstration, that the two binary subsystems which do not present an azeotrope point (i.e. HI and HL binary pairs) are ideal in the liquid phase. After that, we will extend the conclusions to the more general situation in which no ideal behavior is assumed. For the two ideal binary subsystems the excess contribution to the Gibbs energy is zero. The presence of one mbpa in the binary IL pair requires concavity in the $G^{E,L}$ binary curve. This situation has been represented in Fig. 2 where three possibilities are discussed for the $G^{E,L}$ ternary surface: a) concave and with a maximum in a ternary composition, b) concave but without a maximum in a ternary composition, and c) convex. Cases such as that shown qualitatively in Fig. 2a produce a tangent point between the two Gibbs energy functions (G^V and $G^{E,L}$) at the same ternary composition for both liquid and vapor phases, that is to say a ternary azeotrope of minimum boiling point, when temperature increases. However, situations shown in Fig. 2b and 2c are not compatible with the presence of one ternary mbpa

because when the temperature increases, the tangency in the binary LI system occurs first. Pseudoternary planes with a constant ratio $c=x_L/x_I$ are represented in Fig.2d-f for a better visualization. Following, we will show that the NRTL model is not able to produce a situation such as that shown in case a (Fig. 2a and 2d), and consequently the impossibility to reproduce a type #47 of Perry's classification with this equation will be demonstrated.

The $G^{E,L}$ function considering the binary pairs 13 and 23 (LH and IH binary pairs in the previous discussion) as ideal in liquid phase is given by the following equation for the NRTL model:

$$G^{E,L} = \frac{g^{E,L}}{RT} = x_1 x_2 \left(\frac{\tau_{21} G_{21}}{x_1 + G_{21} x_2 + x_3} + \frac{\tau_{12} G_{12}}{G_{12} x_1 + x_2 + x_3} \right) \tag{6}$$

since

$$\tau_{13} = \tau_{31} = 0 \qquad \tau_{23} = \tau_{32} = 0 \qquad \Rightarrow \qquad G_{13} = G_{31} = 1 \qquad G_{23} = G_{32} = 1$$

The total derivative of this function can be written as

$$dG^{E,L} = \frac{\partial G^{E,L}}{\partial x_1} dx_1 + \frac{\partial G^{E,L}}{\partial x_2} dx_2 + \frac{\partial G^{E,L}}{\partial x_3} dx_3 \tag{7}$$

Taking into account the relation between the molar fractions $x_1 + x_2 + x_3 = 1$, and consequently $dx_3 = -dx_1 - dx_2$, Eq. (7) can be written as:

$$dG^{E,L} = \left(\frac{\partial G^{E,L}}{\partial x_1} - \frac{\partial G^{E,L}}{\partial x_3} \right) dx_1 + \left(\frac{\partial G^{E,L}}{\partial x_2} - \frac{\partial G^{E,L}}{\partial x_3} \right) dx_2 \tag{8}$$

The existence of any critical point in the $G^{E,L}$ function implies that the total derivative of that function is zero. This condition can be alternatively formulated by means of the two conditions in Eq (9) and Eq (10).

$$\left(\frac{\partial G^{E,L}}{\partial x_1} - \frac{\partial G^{E,L}}{\partial x_3} \right) = 0 \tag{9}$$

$$\left(\frac{\partial G^{E,L}}{\partial x_2}-\frac{\partial G^{E,L}}{\partial x_3}\right)=0 \tag{10}$$

When these two last equations are satisfied simultaneously Eq. (11) must be also true

$$\frac{\partial G^{E,L}}{\partial x_1}+\frac{\partial G^{E,L}}{\partial x_2}-2\frac{\partial G^{E,L}}{\partial x_3}=0 \tag{11}$$

Using the expression given in Eq. (6) to calculate the partial derivatives indicated in Eq. (11) the following expression is obtained

$$\begin{aligned}\frac{\partial G^{E,L}}{\partial x_1}+\frac{\partial G^{E,L}}{\partial x_2}-2\frac{\partial G^{E,L}}{\partial x_3} &= (x_1+x_2)\left(\frac{\tau_{21}G_{21}}{x_1+G_{21}x_2+x_3}+\frac{\tau_{12}G_{12}}{G_{12}x_1+x_2+x_3}\right)\\ &+x_1x_2\left(\frac{\tau_{21}G_{21}(1-G_{21})}{(x_1+G_{21}x_2+x_3)^2}+\frac{\tau_{12}G_{12}(1-G_{12})}{(G_{12}x_1+x_2+x_3)^2}\right)\end{aligned} \tag{12}$$

Considering that for the binary 1-2 to have one azeotrope of minimum boiling temperature, the $G^{E,L}$ function must be positive for any composition, which means that the term in brackets in Eq. (6) must be positive, it its derived that the first term in the right hand of Eq. (12) is also positive, regardless the sign of the NRTL parameters τ_{12} and τ_{21}. The sign of the second term in the right hand of Eq. (12) must be analyzed for two situations: a) Both binary parameters τ_{12} and τ_{21} are positive, and b) one of them is positive and the other one is negative. The situation in which both parameters are negative is not considered because it would lead to a system involving no binary with minimum boiling point azeotrope as it is required in the type #47 systems. For both a) and b) situations the sign of the second term in the right hand of Eq. (12) is always positive since if $\tau_{ij}<0$ then $G_{ij}>1$ ($(1- G_{ij})<0$) and if $\tau_{ij}>0$ then $G_{ij}<1$ ($(1- G_{ij})>0$). Therefore, the condition given in Eq. (11) cannot be satisfied because the $G^{E,L}$ surface does not present any critical point (i.e. $dG^{E,L}>0$), what implies that no maximum is

possible at any ternary composition preventing the possibility of existence of one ternary minimum boiling point azeotrope (mbpa).

The same conclusion is obtained using an alternative analysis, in which the comparison between the magnitude of the $G^{E,\,L}$ function for the binary and the ternary regions is carried out. To do that, Eq. (6) must be compared with the NRTL equation for a binary system (Eq. (13)) where prime is used for the compositions in the binary region in planes of equal composition of the component 1 (i.e. $x_1=x_{1'}$ and $x_2'=x_2+x_3$ that implies $x_2'>x_2$)

$$G^{E,L} = \frac{g^{E,L}}{RT} = x'_1 x'_2 \left(\frac{\tau_{21} G_{21}}{x'_1 + G_{21} x'_2} + \frac{\tau_{12} G_{12}}{G_{12} x'_1 + x'_2} \right) \tag{13}$$

The product $x_1 \cdot x_2$ is in the binary always higher than $x'_1 \cdot x'_2$ in the ternary region. The second term between brackets is equal in both equations Eq. (6) and Eq. (13), only the first term in brackets remains for this comparison and because $G_{ij}>1$ for $\tau ij<0$ ($Gij<1$ for $\tau ij>0$) is easily checked that for any value of the composition this term takes always higher values for the binary compared with the ternary region. The conclusion is that $G^{E,L}$ values given by Eq. (13) are always higher than those in Eq (6). Consequently, the same conclusion about the impossibility for the NRTL model to present a maximum in the $G^{E,L}$ surface (when one binary subsystem presents a mbpa and the other two binary subsystems are ideal) has been achieved by means of two different arguments used: the analysis of the conditions for the existence of critical points in the $G^{E,L}$ ternary region, and by means of the comparison of the magnitude of the $G^{E,L}$ function in the binary and ternary regions.

For systems type #48 [26], as that represented in Fig. 3a, the situation is similar to that described above. This is because the change in the binary pair with one mbpa (in this case HL unlike type #47) leads to the same conclusion derived for type #47: the NRTL equation is not able to model this type of ternary systems because of the inability to reproduce a $G^{E,L}$ surface with a maximum point at any ternary composition. Because only a convex surface or, in the best case, a concave one but without a ternary maximum point is obtained (Fig. 3b), there is not possibility to obtain the conditions required by the type #48 ternary systems.

Adding ternary interactions

In this section we show that the modification of the classical activity coefficient models by means of the addition of ternary interactions could solve the limitations discussed in the previous section, resulting in the possibility of fitting VLE data for systems such as those of types #47 and #48 [26], used as examples in the present paper.

For example, the addition of the following term to the NRTL model

$$\frac{g^{E,L}}{RT}(\text{ternary interaction}) = x_1 x_2 x_3 \frac{t_1 x_1 + t_2 x_2 + t_3 x_3}{1 + t_4 x_1 x_2 x_3} \tag{14}$$

where t_1, t_2, t_3 and t_4 are fitting parameters, is able to substantially modify the $G^{M,L}$ surface, e.g Eq.(1) for the NRTL model, leading to the topology required by the excess (or mixing) G^{L} and G^{V} functions to satisfy the VLE of many type of systems, as those #47 and #48 discussed in the present paper. The contributions of this modified $G^{M,L}$ function are the following

$$G^{M,L} = \frac{g^{M,L}}{RT} = \frac{g^{Mid,L}}{RT} + \frac{g^{E,L}}{RT}(\text{classical}) + \frac{g^{E,L}}{RT}(\text{ternary interaction}) \tag{15}$$

The analysis of the sign of the total derivative of the $G^{E,L}$ function given by the sum of the classical and ternary interaction contributions, when they are represented by the NRTL equation and Eq.(14), respectively, shows that $dG^{E,L}$ may now take the value zero for a ternary composition depending on the parameter and composition values, even for the less favorable situation in which the two binary subsystems without presence of azeotrope are ideal.

To illustrate this point we show in Fig. 4 an example where both the temperature and the Gibbs energy surfaces versus composition have been represented using the original NRTL equation (Fig. 4a and 4b) and the modified NRTL equation that includes the ternary interaction term (Fig. 4c and 4d). The parameter values that have been used to reproduce these figures are presented in Table 1. The original NRTL parameter values are the same as those used when the additional term to the NRTL equation is added. Fig 4b and 4d have been represented at the temperature of the binary azeotrope and,

consequently, the required topology for to model a type #47 ternary system of Perry's classification [26] implies that the plane for the vapor phase must intersect the surface for the liquid phase. Fig. 4a and 4b show that this fact only occurs for the extended NRTL equation with the ternary contribution and for this reason the ternary azeotrope appears in the T versus composition diagram shown in Fig 4c but not in Fig 4a. These examples illustrate how the modification of the NRTL model is able to reproduce VLE data corresponding to a system of type #47 of Perry's classification [26], involving ternary and binary minimum boiling point azeotropes, which cannot be generated by NRTL equation.

Checking a general case

As already indicated, we have considered in the previous discussion that the two binary subsystems which do not present an azeotrope point (13 and 23 binary pairs) are ideal in the liquid phase. Now we will extend the conclusions to the more general situation in which no ideal pair is assumed. To eventually reach such a behaviors the two binary subsystems with no azeotropic point should present a positive $G^{E,L}$, but not so positive to present a mbpa. The limit of such situation is schematically presented in Fig. 5 and can be expressed by Eq. (16)

$$ln\frac{P_j^0}{P_i^0} = -\left(\tau_{ji}G_{ji} + \tau_{ij}\right) \tag{16}$$

where i represents the L or I component and j = H. This condition has been derived from the slope of the G^V straight line and the value of the first derivative of the $G^{E,L}$ curve at x_L or $x_I \rightarrow 1$. The first member in this equation should be lower than the second one to prevent the presence of a binary mbpa:

$$ln\frac{P_j^0}{P_i^0} < -\left(\tau_{ji}G_{ji} + \tau_{ij}\right) \tag{17}$$

The mathematical demonstration equivalent to the simplified seems not easy since the $G^{E,L}$ surface may now exhibit a maximum. Alternatively we show an example where we

have calculated the T vs. x,y and $G^{E,L}$ vs. z and G^{V} vs. z diagrams for the same system previously considered using the NRTL model but parameters corresponding to the two binary subsystems with no azeotrope in a limit required by Eq. (17).

Fig 6a-d show the equivalent figures to those previously shown in Fig 4a-d but now with the two binary subsystems 1-3 and 2-3 being non-ideal just in a limit imposed by Eq (16), which it can be considered as the highest non-ideality behavior without presence of binary azeotropes. We have analyzed many similar cases with different p_i^0 and τ_{ij} values (always subjected to the described restriction) and we have reached the same conclusion. The observation and comparison of all these figures reveal the incapability of the NRTL model to represent type #47 systems not only for the simplified example shown in Fig 4a and 4b, in which a ternary maximum is not possible for the $G^{E,L}$ surface (as it has been theoretically demonstrated above in this paper), but also for the case shown in Fig 6a and 6b, where it is possible the existence of such maximum due to the high non-ideal contribution of the two non-azeotropic binary pairs. Again, Fig. 6c and 6d show how the addition of a convenient ternary interaction term to the NRTL model avoids this limitation to satisfactorily achieve the modeled of this type of systems in the same way as it was shown in Fig. 4c and 4d for the more simplified case. Intersection areas between the vapor and liquid Gibbs energy surfaces, the last one obtained with the additional term, are evident in both cases represented in Fig. 4d and 6d for the ideal and non-ideal cases, respectively.

From the 125 possible theoretical types of ternary systems presented in the Perry's Handbook of Chemical Engineering [26] regarding the distillation boundaries, for systems involving up to three binary azeotropes and one ternary azeotrope, thirty-six cannot be modeled using the NRTL equation what can be ascertained by analogy with the cases discussed in the present paper. Moreover, seventeen type of systems would have serious difficulties to be correlated and only very restricted cases could be calculated using the classical activity coefficient equations as the NRTL model. The suggested modification should be considered as an example of how modifying the behavior of the $G^{E,L}$ function the required topological condition by the system could be fulfilled. Other possible ternary interactions could be proposed leading to similar or better results. Furthermore, the addition of a ternary interaction contribution to the classical model could not be enough for some specific systems, requiring other modifications of the model (i.e the binary terms) to provide the required greater

flexibility. In conclusion, the modifications of the models taking into account the topological requirements of the Gibbs energy function should be encouraged to achieve better practical results in the experimental equilibrium data correlation. This practice could require a higher number of *adequately selected* parameters, but the number of parameters to be fitted should not be a problem for modern computers.

Conclusions

For a simplified case where the two binary subsystems showing no azeotropy in types #47 and #48 ternary systems [26] were considered as ideal in the liquid phase it has been mathematically demonstrated that the NRTL equation cannot predict such behaviour. In addition, when the NRTL constants corresponding to those binary subsystems are in the limit of presenting azeotropy, it has been tested that the same impossibility persists. It has also been proved that the addition of a ternary term in the $G^{E,L}$ model provides the required flexibility to that function for removing such limitation.

References

[1] Behrens, B.; Eckermann, R. DECHEMA Data Collection. Chemistry Data Series, Dechema, Frankfurt, 1980-1997.

[2] Dormund Data Bank Software Package (DDBSP). Dormund Data Bank Software and Separation Technology Gmbh. 2001.

[3] Frenkel, M.; Dong, Q.; Wilhoit, R.C.; Hall, K.R. TRC SOURCE Database: A Unique Tool for Automatic Production of Data Compilations. Int. J. Thermophys, 22 (2001) 215.

[4] Margules, Sitzber, math.-naturw. K. Kaiserlichen Akad. Wiss. (Vienna) 104 (1895) 1243.

[5] J. J. Van Laar, Z. Phys. Chem. 185 (1929) 35.

[6] H. Renon, J.M. Prausnitz, AIChE J., 14 (1968) 135-144.

[7] D. Abrams, J.M. Prausnitz, AIChE J., 21 (1975) 116-128.

[8] G.M. Wilson, J. Am. Chem. Soc., 86 (1964) 127–130.

[9] J. Rarey, Ind. Eng. Chem. Res. 44 (2005) 7600.

[10] A. Marcilla, M.M. Olaya, M.D. Serrano, J.A. Reyes-Labarta, Fluid Phase Equilibria. 296, (2010) 15 - 24.

[11] R.E. Treybal, Liquid Extraction, first ed., UTEHA, 1968.

[12] A. Marcilla, M. M. Olaya and M. D. Serrano, Ind. Eng. Chem. Res. 50 (2011) 4077 – 4085.

[13] ChemCAD 6.5, Chemstations Inc. 2015.

[14] A. Marcilla, M.M. Olaya, M.D. Serrano, R. Velasco, J.A. Reyes-Labarta, Fluid Phase Equilib. 281 (2009) 85-87.

[15] M.M. Olaya, J.A. Reyes-Labarta, R. Velasco, I. Ibarra, A. Marcilla, Fluid Phase Equilib. 265 (2008) 184-191.

[16] C-C.Chen, P. Mathias, Applied Thermodynamics for Process Modeling. AIChE J. 2002, 48, 194.

[17] S. I. Sandler, Using Aspen Plus® in Thermodynamics Instruction: An step-by-step guide, John Wiley & Sons, Inc., New Jersey, 2015.

[18] S. Gebreyohannes, B.J. Neely, K. A. M. Gasem, Fluid Phase Equilib. 379 (2014) 196−205.

[19] E. Neau, J. Escandell, C. Nicolas, Ind. Eng. Chem. Res. 49 (2010) 7580–7588.

[20] M. Frenkel, Q. Dong, R.C. Wilhoit, K.R. Hall, Int. J. Thermophys. 22 (2001) 215.

[21] A. Vetere, Fluid Phase Equilib. 218 (2004) 33-39.

[22] A. Marcilla, M.M. Olaya, M.D. Serrano, M.A. Garrido, Ind. Eng. Chem. Res., 52 (2013) 13198-13208.

[23] A. Marcilla, J.A. Reyes-Labarta, M.D. Serrano, M.M. Olaya, The Open Thermodynamics Journal. 5 (2011) 48 - 62.

[24] J. Gmehling, U. Onken, Vapor-Liquid Equilibrium Data Collection. Chemistry Data Series; Vol. I-1, DECHEMA: Frankfurt, 1977.

[25] A. Marcilla, M.M. Olaya, J.A. Reyes-Labarta, Fluid Phase Equilibria (2015), http://dx.doi.org/10.1016/j.fluid.2015.12.047 (article in press).

[26] D.W. Green, R.H. Perry, “Perry’s Chemical Engineers’ Handbook”. 7th ed. McGraw-Hill. 2007.

Table 1. Parameters corresponding with Fig. 4 (simplified case), where both the classical and extended NRTL models have been used to formulate the Gibbs energy of excess for the liquid phase.

	Antoine equation constants (*)		
component	A	B (ºC)	C (ºC)
1	8.76	2000	253
2	7.90	1600	225
3	8.35	1700	230
NRTL parameters (K)		Ternary interaction parameters	
A_{12}	200	t_1	11
A_{21}	200	t_2	6
A_{13}	0.0	t_3	5
A_{31}	0.0	t_4	30
A_{23}	0.0		
A_{32}	0.0		
$\alpha_{12} = \alpha_{13} = \alpha_{23}$	0.2		

(*) Antoine equation: $\log p(mmHg) = A - \frac{B}{T + C}$

Table 2. Parameters corresponding with Fig. 6 (non-ideal case), where both the classical and extended NRTL models have been used to formulate the Gibbs energy of excess for the liquid phase.

	Antoine equation constants (*)		
component	A	B (ºC)	C (ºC)
1	8.76	2000	253
2	7.90	1600	225
3	8.35	1700	230
NRTL parameters (K)		Ternary interaction parameters	
A_{12}	200	t_1	11
A_{21}	200	t_2	6
A_{13}	39	t_3	5
A_{31}	50	t_4	30
A_{23}	130		
A_{32}	50		
$\alpha_{12} = \alpha_{13} = \alpha_{23}$	0.2		

(*) Antoine equation: $\log p(mmHg) = A - \frac{B}{T + C}$

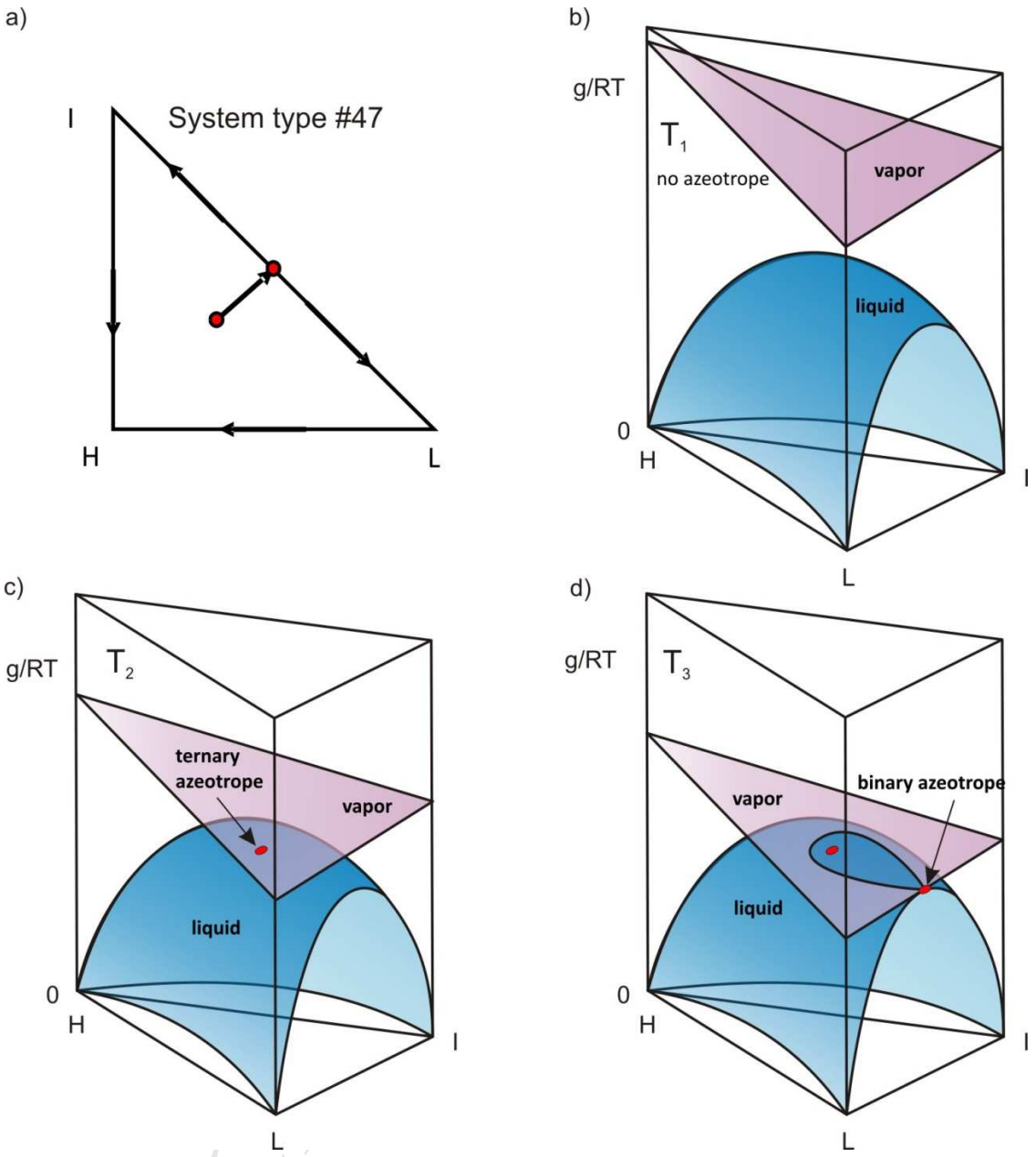

Fig. 1. System type #47 [26], ternary minimum boiling point azeotrope (ternary mbpa) and a binary minimum boiling point azeotrope (IL binary mbpa): a) Distillation region diagram, b-d) Vapor and liquid Gibbs energy surfaces at different temperatures ($T_1<T_2<T_3$) showing the situations where the ternary and binary azeotropes are present.

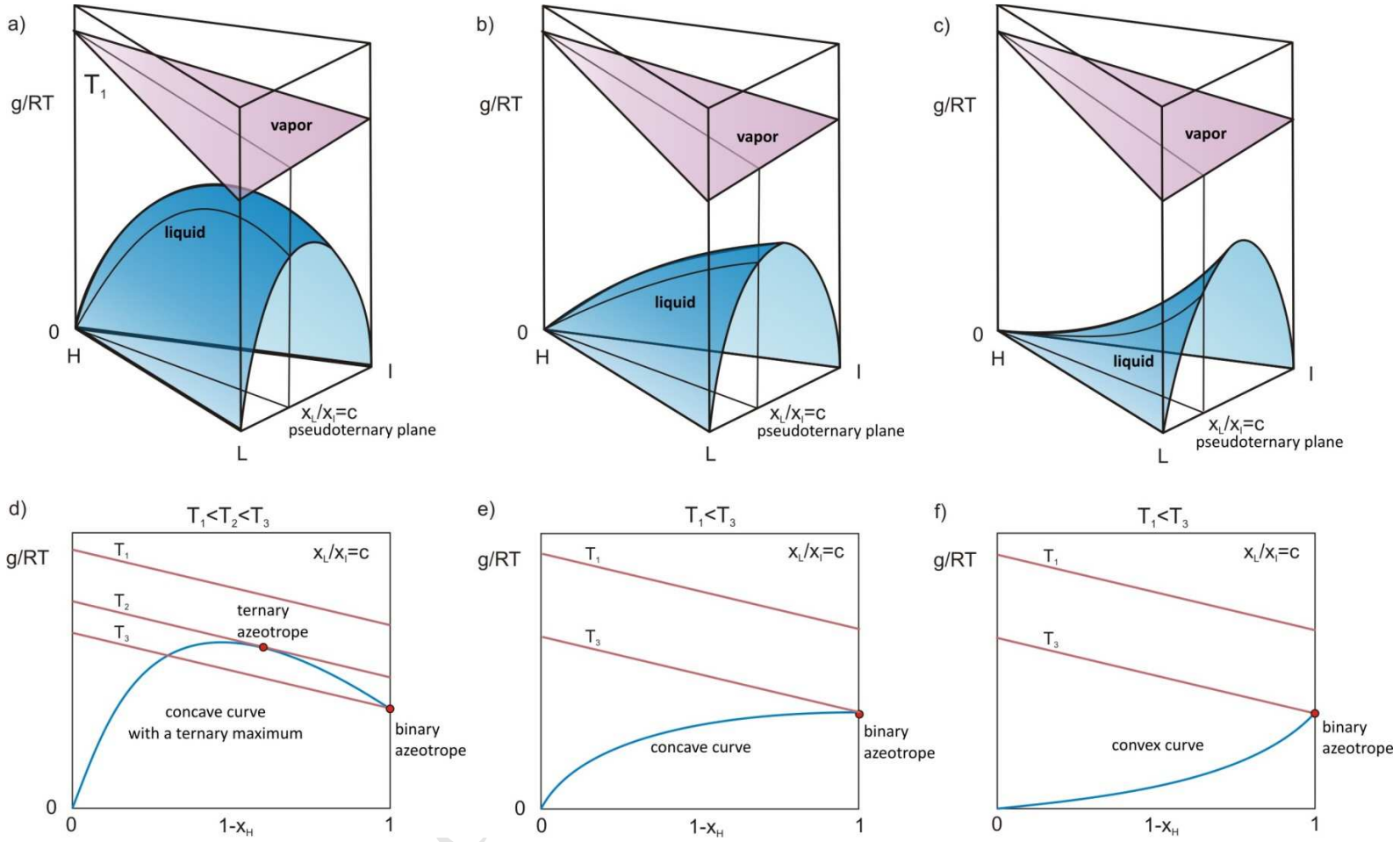

Fig. 2. Vapor and liquid Gibbs energy surfaces showing three possibilities for the $G^{E,L}$ surface: a) concave with a maximum in a ternary composition, b) concave (without a ternary maximum), and c) convex. Pseudoternary planes with a constant ratio $c=x_L/x_I$ are represented in d-f), respectively.

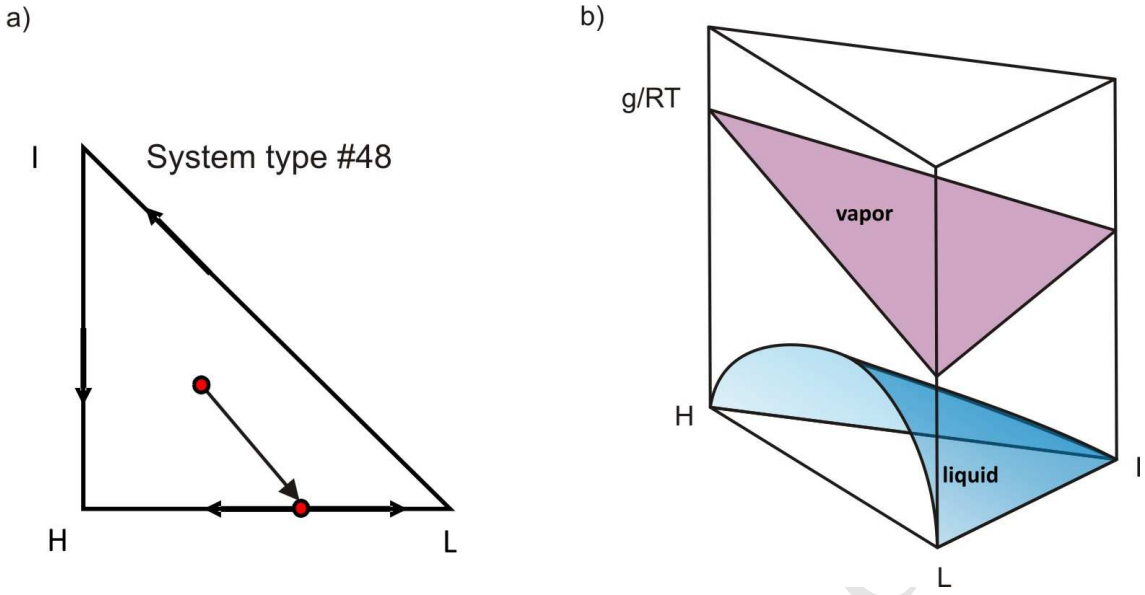

Fig. 3. System type #48 [26], ternary minimum boiling point azeotrope (ternary mbpa) and a binary minimum boiling point azeotrope (LH binary mbpa): a) Distillation region diagram, and b) vapor and liquid Gibbs energy surfaces at low temperature (lower than ternary and binary mbpa).

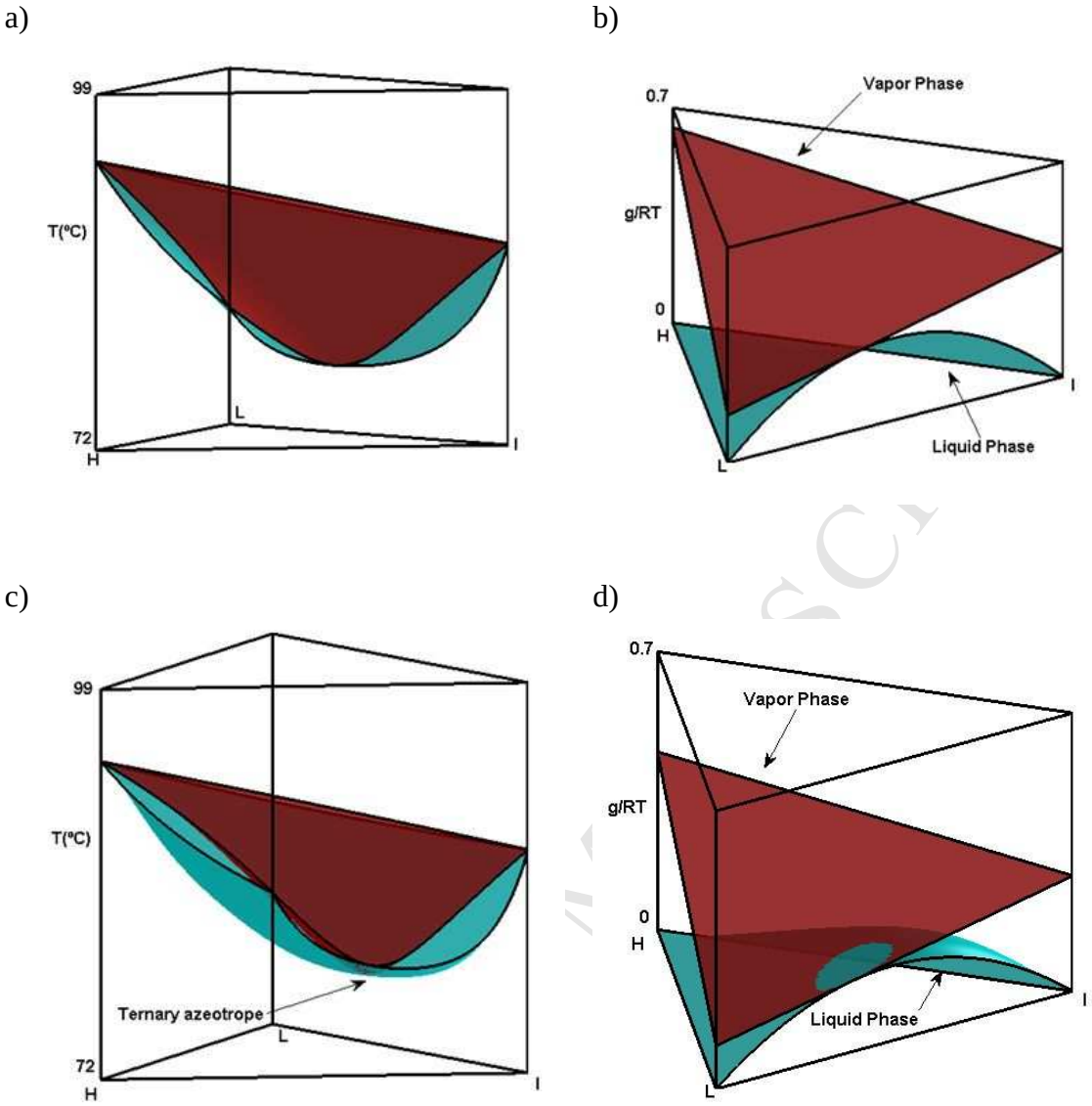

Fig. 4. Temperature versus composition and Gibbs energy surfaces (vapor and liquid) for a ternary system with a binary minimum boiling point azeotrope (1-2) and two ideal binary subsystems (1-3 and 2-3) using both: a, b) the NRTL model, and c, d) the extended NRTL model. Parameters for the liquid and vapor phases are in Table 1. Gibbs energy representations are at the temperature of the binary azeotrope (350K).

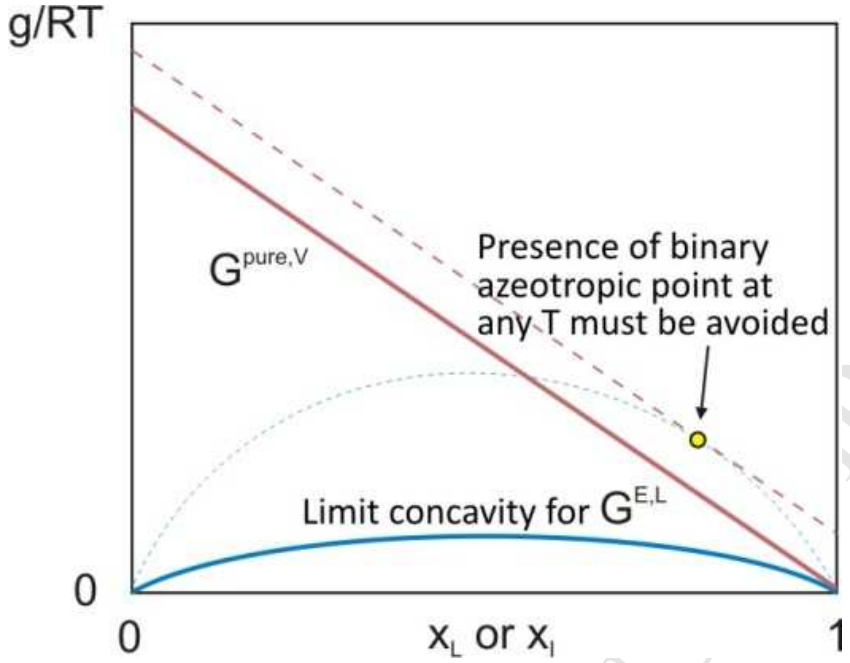

Fig. 5. Analysis of the limit situation in the concavity of the $G^{E,L}$ function for non-ideal HL and HI binary pairs without azeotrope, related to the slopes of the vapor and liquid functions at the more-volatile component (L or I).

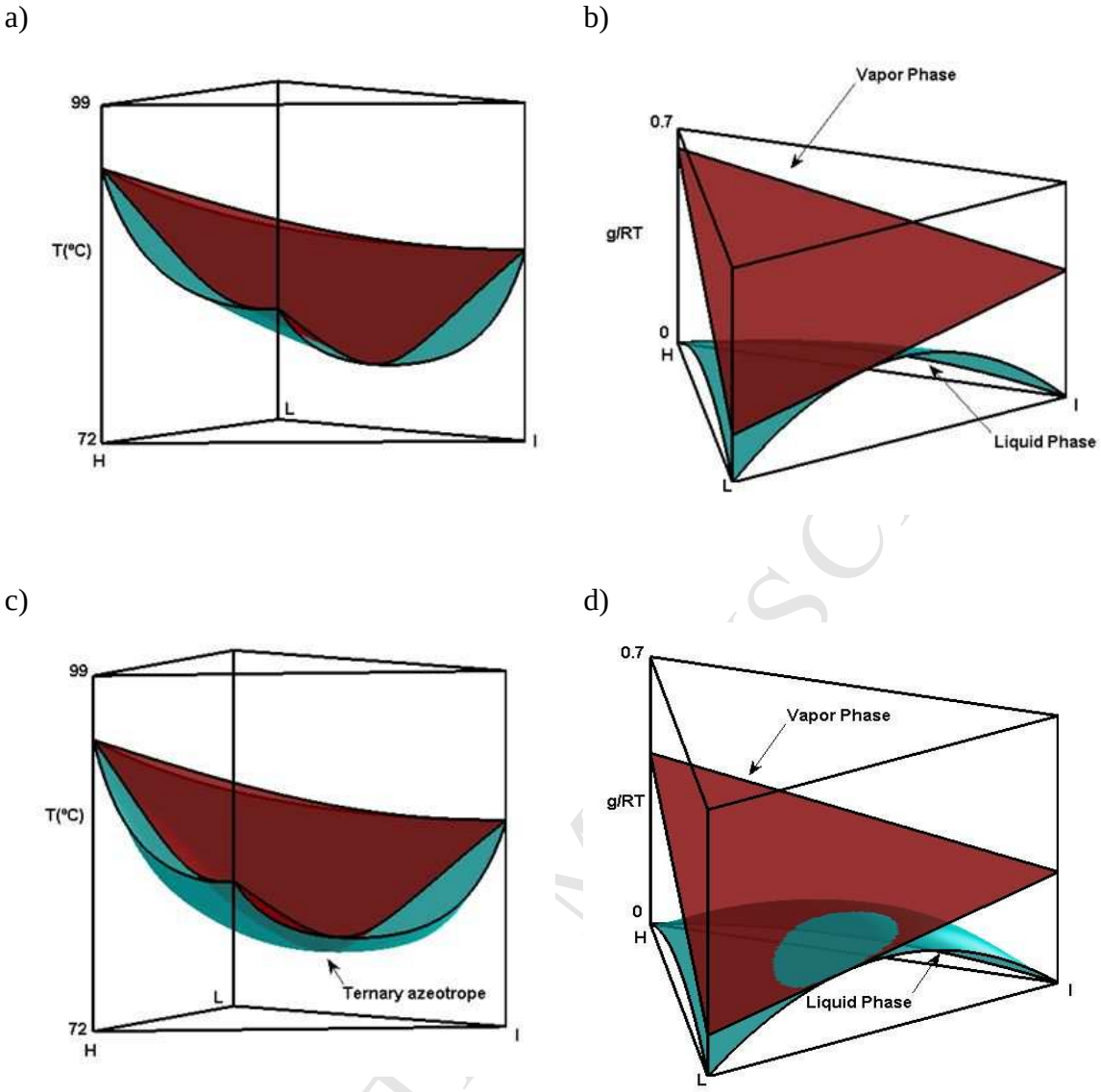

Fig. 6. Temperature versus composition and Gibbs energy surfaces (vapor and liquid) for a ternary system with a binary minimum boiling point azeotrope (1-2) and two non-ideal binary subsystems (1-3 and 2-3) using both: a, b) the NRTL model, and c, d) the extended NRTL model. Parameters for the liquid and vapor phases are in Table 2. Gibbs energy representations are at the temperature of the binary azeotrope (350K).